

5.1 Introduction

There is increasing demand for the lead –free solder alloys with low melting point. These low melting alloys are manufactured from the low melting point metals. The lead in the conventional solder alloy is very dangerous due to its toxic nature. It is harmful for the environment because lots of PCBs and electronic equipment are recycled from the dumps. The European countries, the US and Japan are planning to ban the use of lead in many applications including soldering. They are looking for the lead-free solder alloys. The evaluation of properties of the lead-free solder is very important as far the applications are concerned. The properties of the new solder alloys should be comparable with the properties of the conventional Pb-Sn eutectic solder alloy. The Government should come up with some strict policies to handle the issues like proper handling of waste materials and to ban the use of lead. In many countries the ban of lead is going to be imposed within a certain time frame. Lead is already banned in the applications like pain, plumbing and gasoline.

The next concern is waste treatment in manufacturing. The wastes generated from the soldering are solder, solder dross, wipes and packaging containers. Some waste can be economically recycled for its value and others are disposed as waste which is harmful for the environment. During cleaning of recycling waste, lots of leads are present in the effluent liquid. The reason for the recent concern is that a great number of products are being disposed in landfills, products such as televisions, radios, games and other products available to the consumer, and potential solder from these products is leaching into municipal water supplies.

A lead-free solder database will have to be created, and it should be the basis for developing new lead-free solder alloys. The database will help us to avoid complex and time consuming experiments. Information on thermodynamic properties such as

mixing enthalpies is essential for thermodynamic optimization of phase diagrams, for the development of lead-free solder database, and for the predicting physical and chemical properties, such as surface tension and viscosity. From the literature survey, it is observed that lead cannot be substituted by any single metal in the conventional lead-tin solder to have desirable properties of the targeted materials. So many efforts have been made to use more than one metal in the lead-free solder alloys. The systems may be ternary or higher order metallic systems like Bi-In-Sn, In-Sn-Zn, and In-Bi-Sn-Zn.

The elf measurements provide the accurate results for the activities of the components in the multicomponent solution. It does not give accurate results for the enthalpies of mixing. That is why the calorimetric measurements of this ternary system are important as far as the measurements of accurate enthalpy of mixing are concerned.

Therefore, the authors have carried out the calorimetric investigations of the In-Sn-Bi ternary system along three of the cross sections varying indium content along each of the cross section, using drop calorimetric technique at various temperatures of 767, 813 and 855 K. Indium has been dropped into the Bi-Sn alloys at a regular interval of time. MHTC 96 line Evo (Seta ram, France) calorimeter has been used for the enthalpy measurements. Partial and integral enthalpies of mixing have been calculated from the calorimetric data. Isoenthalpy curves were plotted for the integral enthalpy of mixing. The experimental data were treated with the theoretical Redlich - Kister- Muggianu substitutional solution model to derive the ternary interaction parameter by least square fitting method.

5.2 Literature review

Differential Scanning Calorimetry (D.S.C.) techniques have been used to measure the Bi activity and mixing enthalpies in Bi-Sn-In system by Brunetti et al. [Brunetti et al. (2006)]. The results shown that this ternary system at fixed Bi composition, $x_{Bi} = 0.20$, and 565K behaves as a non-ideal system with exothermic $\Delta_{mix} H_T^o$ passing through a minimum at $x_{In} = 0.58$ and $x_{Sn} = 0.22$. In the whole range of the quantity $x_{Sn}/(x_{Sn}+x_{In})$ and at 1050 K the average value of the bismuth activity is 0.14 ± 0.02 which implies an average activity coefficient of Bi equal to 0.70 ± 0.01 . The Bi activity in ternary alloys at 1000 K with variable x_{Bi} and fixed ratio $\rho = x_{Sn}/x_{In} = 0.85$ has been measured. The excess integral free energy change for the mixing, $\Delta_{mix} G_T^o(xs)$, has also been evaluated by making use of both the torsion-effusion experimental and literature data for Bi-Sn and Bi-In binary systems. Under these conditions, the ternary system is not a regular solution and the entropy contribution to the free energy of mixing is dominating the Gibbs energy.

Thermodynamic properties like transition temperature, as well as latent heat of melting of 29 alloys from the Bi-In-Sn system was investigated using Perkin-Elmer DSC-7 instrument by Witusiewicz et al. [Witusiewicz et al. (2008)]. A new thermodynamic explanation is made for the ternary Bi-In-Sn system in the entire composition range. The parameters required for the thermodynamic models of the boundary binary systems Bi-In, Bi-Sn and In-Sn are taken from previous assessments, and those for the Bi-In-Sn system are taken after optimization in this study using phase equilibria and the enthalpy of melting data of different alloys available in the literature and measured in the present work. Using thermodynamic explanation, various phase equilibrium data and thermodynamic properties are computed. The calculated data are compared against the experimental data and found reasonably good agreement. Tie-line compositions

were obtained from the analysis of the chemical composition of the phases in equilibrium, using energy dispersive X-ray analysis (EDX): (Bi)–In–(Sn) at 77°C, BiIn₂–β–γ at 59°C including the composition of the liquid phase at 59°C and the tie-line BiIn₂–γ at 59°C [Witusiewicz et al. (2008)].

Miscibility gap in the Bi–Sn–Zn system was studied using DTA/DSC and RT/HT-XRD. Miscibility gap in the Bi-Zn binary is well established but not in the ternary Bi-Sn-Zn. For the first isopleths with w (Bi) ~10% and w (Sn) ~5%, 13% and 19% composition was used for the measurement of enthalpy by DTA/DSC with the objectives of determining the miscibility gap in the liquid phase. For the second isopleths having composition of w(Sn) ~ 40%, 58%, 77/81% and w(Zn) ~ 12% were also used obtain enthalpy data by DTA/DSC to complete the study of Bi–Sn–Zn. Solubility in the terminal solid solutions were characterized by SEM/EDS. To verify the DTA / DSC results samples were also characterized by RT-XRD and HT-XRD (High Temperature X-Ray Diffraction) for solid state phase equilibria By Braga et al. [Braga et al. (2007)].

Thermodynamic investigations of liquid Bi–In–Zn alloys were carried out at 500°C by a drop calorimetric technique using a Calvet- type micro calorimeter by Zuoan Li et al. [Zuoan et al. (2007)]. Calorimetric measurements of liquid In–Sn and In–Sn–Zn alloys have been carried out by Sabbar et al. [Sabbar et al. (2010)]. Thermodynamic investigations by drop calorimetric technique for Ag-Ca liquid alloys at temperatures (1254 and 1131) K using a Seta ram MHTC 96 Line evo calorimeter have been carried out By Debski et al. [Debski and Gasior (2014)]. This Measurements were conducted for alloys of concentrations between 0.0642 ≤ X_{Ca} ≤ 0.9396 at T = 1254 K and at 1131 K between 0.7564 ≤ X_{Ca} ≤ 0.9647. The results obtained are negative in the entire range of compositions. The minimum of the integral enthalpy of mixing equals to –24609

J/mol of atoms was observed for 0.4634 mol fraction of calcium at $T = 1254$ K. From the experimental results it was observed that $\Delta_{\text{mix}}H$ of Ag–Ca liquid alloys is almost independent of temperature and that too they are almost twice less exothermic than those ones by vapour pressure measurements. The heat of solution of Ge and Te in liquid Ge-Te alloy and of Si in liquid Si-Te alloys was measured in a heat flow calorimeter at different temperatures by Schlieper et al. [Schlieper and Blachnik (1996)]. The enthalpies of formation of (Ru) hcp solid solution and Mo_5Ru_3 (phase) in the Mo-Ru system and ternary extension in the Mo-Ru-Si system at $\text{Mo}_{56}\text{Ru}_{37}\text{Si}_7$ composition, have been obtained by high-temperature direct reaction synthesis calorimetry at 1760K by Benarchid et al [Benarchid et al. (2009)].

Calorimetric investigations of liquid Cu-In-Sn alloys were carried out at 1073K by Zuoan Li et al. [Zuoan Li et al. (2006)]. They have used drop calorimetric technique using a Calvet-type microcalorimeter. The experimental results were optimized based on the Redlich-Kister-Muggianu model and same can be used in lead free solder database. The measurements were carried out at different temperatures. It has been observed that the enthalpies of mixing of liquid ternary system are temperature dependant. It is clearly shown that thermodynamic data of this system was very useful for CALPHAD. Calorimetric investigations of molten ternary Co-Sb-Sn alloys were carried out using high temperature drop calorimetry by Elmahfoudi et al. [Elmahfoudi et al. (2012)]. The measurements have been done along five sections, $x_{\text{Sb}}/x_{\text{Sn}} = 1:1$, $x_{\text{Sb}}/x_{\text{Sn}} = 1:3$, $x_{\text{Sb}}/x_{\text{Sn}} = 3:1$, $x_{\text{Co}}/x_{\text{Sn}} = 1:4$, and $x_{\text{Co}}/x_{\text{Sb}} = 1:5$ at 1273 K.

In the same year Jendrzeczyk-Handzlik [Jendrzeczyk-Handzlik et al. (2012)] has carried out calorimetric measurements of liquid Au-Sb-Sn alloys. The experiment was designed along three cross sections at the temperatures: 923 and 1078 K. Experimental data were fitted with the expression obtained for the ternary enthalpy of mixing from

binary interaction parameters in R-K polynomials. The difference in both experimental and R-K polynomials is the contribution from ternary interactions, and a full set of parameters describing the concentration dependence were reported. The enthalpy of the mixing as a function of compositions was also derived at both the temperatures. Exothermic heat of mixing for the ternary system was observed for entire compositions. The enthalpy of mixing was found to be independent of temperature in the range of temperatures of investigations. Many authors [Benarchid, et al. (2009), and Fimaa, et al. (2009)] have worked on different system on this instrument.

5.3 Experimental

5.3.1 Materials

High purity metals (In, Bi, Sn) were used to form alloys. α -Al₂O₃ sapphire obtained from Johnson Matthey, U. K were used as calibration standard. In order to form Bi-Sn alloys, Bi pellets and Sn shots were sealed under vacuum in a quartz tube and heated it at 723 K for 48 hours with intermediate shaking and finally, quenching in water. Fine sandpaper was used to remove the oxide layer on the surface of Indium ingot. All the pure metals and chemicals were used as supplied and listed in Table 5.1.

Table 5.1 Purities and sources of materials used in the present study

Materials	Source	Initial purity (wt. %)
Indium (ingot)	Johnson Matthey, UK	99.999
Tin (shots)	Johnson Matthey, UK	99.999
Bismuth(lumps)	Johnson Matthey, UK	99.999
Argon gas	Indian oxygen limited, India	>99

MHTC 96 line evo drop calorimeter (Seta ram, France) was used in this study for ternary systems. It has a thermopile of 20 (pt-ptRh10) S-type thermocouples. It has a continuous water cooled graphite tube resistance furnace. The maximum operating temperature of the furnace is up to 1320°C. In order to drop the sample into the crucible

automatically, there is a provision of motorized dropping device. Calorimeter was calibrated by dropping α -Al₂O₃ sapphire at the end of each experiment. These needles meet NIST (National Institute of Standards and Technology, Gaithersburg, USA) standard specifications. The temperature of the sample dispenser was controlled by constantan-copper thermocouple before each drop. The calorimeter is totally controlled by CALISTO software. Before the start of the experiments a certain quantity of binary alloy was taken in the calorimeter crucible (length 60 mm, outer diameter 12 mm). It was used as the solvent for the metal to be dropped from the sample dispenser. The water cooling system and flow of gas was controlled by the CALISTO software. The heating rate, holding time, cooling rate of the furnace and gas flow rate was programmed before the start of the experiments. At the beginning of experiment, protection tube was evacuated and flushed with high-purity argon (99.9999 vol. %). The oxidation of the alloy was prevented by the continuous flow of argon (approx. 30 ml/min) during the experiments. Weight of the crucible with the sample before and after the experiment was measured to assess the weight loss. The weight loss was found to be negligible. The recorded heat signals returned to the base line after 30 minutes of the indium drop and 25 minutes after the α -Al₂O₃ addition. The recorded heat signals returned to the base line after 30 minutes of the indium drop and 25 minutes after the α -Al₂O₃ addition. The observed signal shows like peaks. These peaks are labeled for convenience. The peaks obtained during the simultaneous drops of Indium at regular intervals. The area of these peaks represent the change in enthalpies of dropped sample from drop temperature to calorimeter temperature including the rise in temperature, melting, phase transformations and also the change in enthalpy during mixing of ternary system. The area of the individual peaks is calculated using Base-line Integration option available in the math tab on top menu of the Calisto Processing

software provided by the manufacturer. By selecting starting and end points of the peaks area is automatically calculated and displayed on the screen in a box.

In this study the calorimetric measurements were carried out for Bi-In-Sn system along three sections of $x_{\text{Sn}}/x_{\text{Bi}}$ ratio 1/2, 1 and 2 at 767, 813 and 855 K. Reproducibility of the data were checked by repeating the experiments at the above temperatures once more.

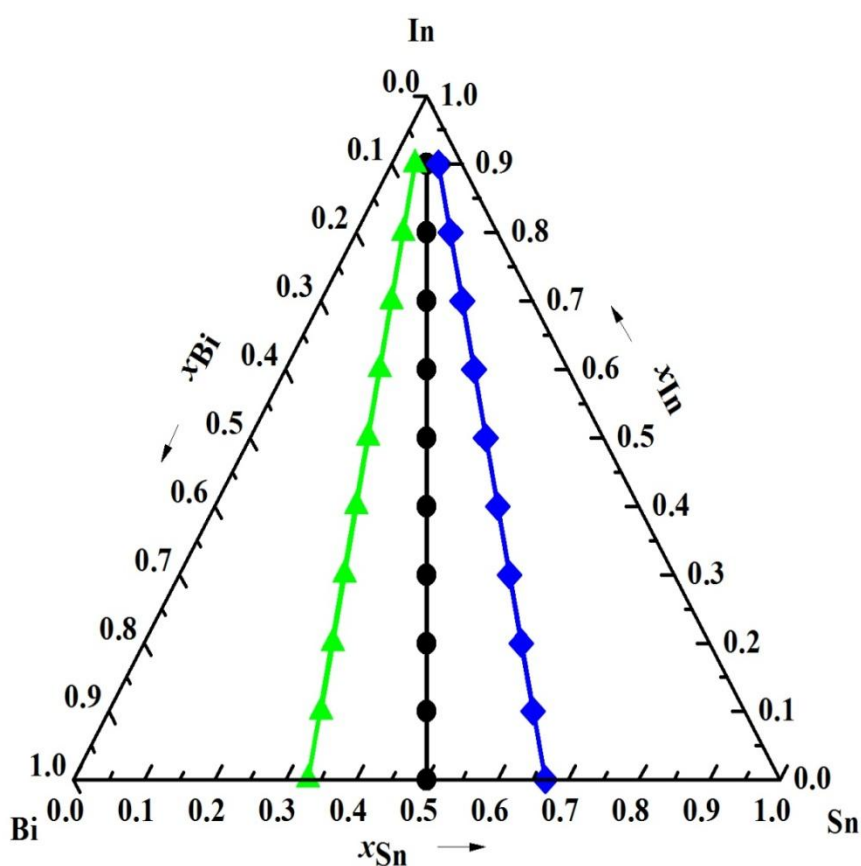


Figure 5.1 Compositions of the investigated cross sections along which mixing enthalpy were measured at three cross-sections: $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$; ▲, $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x}\text{In}_x$; ●, $(\text{Sn}_{0.67}\text{Bi}_{0.33})_{1-x}\text{In}_x$; ■.

5.4 Result and discussion

The heat flow data as a function of temperature were recorded by CALISTO Data Acquisition. Then, the heat flow curves were integrated to obtain the area of the peaks by the CALISTO Data Processing software. The measured enthalpy ($\Delta H_{Reaction,In,i}$) after the integrations of the heat flow curves is calculated by Equation. (2.25).

The partial enthalpy ($\Delta \bar{H}_{In,i}^m$) and integral enthalpy ($\Delta_{mix}H$) were calculated by Equations (2.26) and (2.27) respectively.

It were calculated along the cross-sections $x_{Sn}/x_{Bi}=0.5$, $x_{Sn}/x_{Bi}=1$, $x_{Sn}/x_{Bi}=2$ at 767, 813 and 855 K by varying the composition of In for entire composition of indium. The values of integral enthalpy and partial enthalpy of mixing along the cross-sections $x_{Sn}/x_{Bi}=0.5$, $x_{Sn}/x_{Bi}=1$ and $x_{Sn}/x_{Bi}=2$ are shown in Table 5.2. Figures 5.2- 5.4 shows graphical representation composition of indium (x_{In}) as abscissa and the integral enthalpy of mixing as ordinate. The values of $\Delta_{mix}H$ binary Bi-Sn were taken from the data in chapter 4.

Table 5.2 Integral enthalpy of mixing resulting from calorimetric measurements of Bi-In-Sn system with tin dropped at 767, 813 and 855 K. Standard states: pure liquid metals

No. of moles of Indium n_{In} (mol)	Mole fraction (x_{In})	Standard uncertainties $u(x_{In})$	Heat effect $\Delta H_{Signal} \cdot K$ (J)	Standard uncertainties $\Delta H_{Signal} \cdot K$ (J)	Heat of Reaction $\Delta H_{Reaction}$ (J)	Partial enthalpy $\bar{\Delta H}$ (J mol ⁻¹)	Integral enthalpy $\Delta_{mix}H$ (J mol ⁻¹)
Series 1: (Sn _{0.33} Bi _{0.67}) _{1-x} In _x alloys; Atmosphere : Argon at pressure p = 0.1MPa, starting amount $n_{Bi} = 0.002088$ mol, $n_{Sn} = 0.00104$ mol, $K = 0.00367$ J μVs^{-1} , $T_D = 298$ K, $T_M = 767$ K, $\Delta_{mix}H_{Bi-Sn} = 90.13$ J mol ⁻¹ , $H_{In}^{T_D \rightarrow T_M} = 16906.14$ (J mol ⁻¹) [Kubaschewski and Alcock (1979)]							
0.000340	0.0980	0.0001	4.147	0.01	-1.601	-4709	-380.4
0.000508	0.2133	0.0001	6.561	0.01	-2.027	-3990	-841.6
0.000545	0.3081	0.0001	7.398	0.01	-1.815	-3330	-1142

0.000783	0.4103	0.0001	11.26	0.02	-1.976	-2524	-1346
0.000880	0.4942	0.0001	13.27	0.02	-1.602	-1820	-1413
0.001687	0.6026	0.0002	26.33	0.05	-2.19	-1298	-1389
0.002927	0.7103	0.0001	47.16	0.10	-2.32	-792.6	-1227
0.005452	0.8075	0.0002	89.83	0.20	-2.334	-428.1	-959.0
0.005351	0.8552	0.0001	88.93	0.20	-1.535	-286.9	-792.5
0.005453	0.8844	0.0001	91.55	0.20	-0.637	-116.8	-656.3
0.005417	0.9037	0.0001	90.97	0.20	-0.607	-112.1	-565.5
Series 2: $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$ alloys; Atmosphere : Argon at pressure $p = 0.1\text{MPa}$, starting amount $n_{\text{Bi}} = 0.002088\text{ mol}$, $n_{\text{Sn}} = 0.00104\text{ mol}$, $K = 0.00327\text{ J } \mu\text{Vs}^{-1}$, $T_{\text{D}} = 298\text{ K}$, $T_{\text{M}} = 813\text{ K}$, $\Delta_{\text{mix}}H_{\text{Bi-Sn}} = 94.15\text{ J mol}^{-1}$, $H_{\text{In}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 18249.02\text{ (J mol}^{-1}\text{)}$ [Kubaschewski and Alcock (1979)]							
0.000361	0.1035	0.0002	5.095	0.01	-1.493	-4136	-343.5
0.00047	0.2099	0.0001	6.773	0.01	-1.804	-3838	-758.4
0.000497	0.2980	0.0001	7.394	0.01	-1.676	-3372	-1050
0.000932	0.4195	0.0001	14.66	0.03	-2.348	-2519	-1304
0.000875	0.5006	0.0001	14.44	0.03	-1.528	-1746	-1366
0.001993	0.6211	0.0002	34.14	0.08	-2.232	-1120	-1307
0.002349	0.7050	0.0001	41.21	0.09	-1.658	-705.8	-1173
0.005132	0.8012	0.0002	91.52	0.21	-2.134	-415.8	-926.4
0.00532	0.8515	0.0001	96.13	0.22	-0.956	-179.7	-737.7
0.005463	0.8821	0.0001	99.14	0.24	-0.553	-101.2	-606.6
0.005447	0.9021	0.0001	98.93	0.23	-0.470	-86.29	-518.0
Series 3: $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$ alloys; Atmosphere : Argon at pressure $p = 0.1\text{MPa}$, amount $n_{\text{Bi}} = 0.002088\text{ mol}$, $n_{\text{Sn}} = 0.00104\text{ mol}$, $K = 0.00333\text{ J } \mu\text{Vs}^{-1}$, $T_{\text{D}} = 298\text{ K}$, $T_{\text{M}} = 855\text{ K}$, $\Delta_{\text{mix}}H_{\text{Bi-Sn}} = 96.44\text{ J mol}^{-1}$, $H_{\text{In}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 19473.15\text{ (J mol}^{-1}\text{)}$ [Kubaschewski and Alcock (1979)]							
0.000347	0.0999	0.0001	5.430	0.01	-1.327	-3824	-295.1
0.000432	0.1994	0.0002	6.863	0.01	-1.549	-3586	-658.9
0.000629	0.3104	0.0001	10.22	0.02	-2.025	-3219	-1014
0.000871	0.4215	0.0001	14.96	0.03	-2.005	-2302	-1221
0.000983	0.5105	0.0002	17.47	0.04	-1.671	-1700	-1295
0.001596	0.6083	0.0001	29.35	0.08	-1.733	-1086	-1253
0.002811	0.7103	0.0001	52.94	0.13	-1.802	-641.1	-1094
0.004488	0.7954	0.0002	85.87	0.22	-1.517	-338.0	-871.9
0.004655	0.8431	0.0002	89.68	0.21	-0.958	-205.8	-716.4
0.003976	0.8692	0.0001	77.28	0.21	-0.151	-37.98	-603.6
0.004263	0.8890	0.0001	82.66	0.20	-0.354	-83.04	-524.9
0.004163	0.9033	0.0001	81.32	0.22	0.251	60.39	-449.5
Series 4: $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x}\text{In}_x$ alloys; Atmosphere : Argon at pressure $p = 0.1\text{MPa}$, starting amount $n_{\text{Bi}} = 0.001699\text{ mol}$, $n_{\text{Sn}} = 0.001699\text{ mol}$, $K = 0.00374\text{ J } \mu\text{Vs}^{-1}$, $T_{\text{D}} = 298\text{ K}$, $T_{\text{M}} = 767\text{ K}$, $\Delta_{\text{mix}}H_{\text{Bi-Sn}} = 122.26\text{ J mol}^{-1}$, $H_{\text{In}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 16906.20\text{ (J mol}^{-1}\text{)}$ [Kubaschewski and Alcock 91979)]							
0.000405	0.1065	0.0001	5.481	0.01	-1.366	-3373	-250.0
0.000443	0.1997	0.0001	6.359	0.02	-1.13	-2551	-490.0
0.000619	0.3015	0.0002	9.017	0.02	-1.448	-2339	-725.3
0.001005	0.4211	0.0002	14.78	0.04	-2.213	-2202	-978.1
0.001108	0.5130	0.0002	17.06	0.04	-1.675	-1512	-1063

0.001712	0.6090	0.0002	26.88	0.07	-2.066	-1207	-1091
0.00261	0.6993	0.0001	42.49	0.11	-1.637	-627.2	-984.0
0.005447	0.7971	0.0002	90.11	0.23	-1.975	-362.6	-781.9
0.005346	0.8462	0.0001	89.37	0.23	-1.011	-189.1	-638.5
0.00542	0.8765	0.0001	91.38	0.23	-0.253	-46.68	-521.9
0.004909	0.8952	0.0002	82.85	0.22	-0.14	-28.52	-447.2
0.004153	0.9071	0.0001	70.13	0.18	-0.083	-19.99	-398.7
Series5: (Sn _{0.50} Bi _{0.50}) _{1-x} In _x alloys; Atmosphere : Argon at pressure p = 0.1MPa, starting amount n _{Bi} = 0.001699 mol, n _{Sn} = 0.001699 mol, K = 0.00318 J μVs ⁻¹ , T _D = 298 K, T _M = 813 K, Δ _{mix} H _{Bi-Sn} = 126.85 J mol ⁻¹ , H _{ln} ^{T_D→T_M} = 18249.02 (J mol ⁻¹) [Kubaschewski and Alcock (1979)]							
0.000358	0.0953	0.0001	5.412	0.01	-1.121	-3131	-183.7
0.000525	0.2063	0.0001	8.324	0.02	-1.257	-2394	-454.8
0.000654	0.3114	0.0001	10.38	0.02	-1.554	-2376	-709.4
0.000764	0.4038	0.0001	12.28	0.03	-1.664	-2178	-906.3
0.001073	0.4982	0.0001	17.86	0.04	-1.72	-1603	-1017
0.001817	0.6044	0.0001	30.89	0.07	-2.268	-1248	-1066
0.00326	0.7132	0.0001	57.84	0.14	-1.652	-506.7	-911.9
0.005542	0.8046	0.0002	99.26	0.24	-1.88	-339.2	-729.4
0.005492	0.8515	0.0002	99.97	0.24	-0.251	-45.70	-565.3
0.005988	0.8823	0.0002	109	0.24	-0.271	-45.26	-457.4
0.005076	0.8999	0.0001	92.82	0.25	0.192	37.83	-383.4
Series 6: (Sn _{0.50} Bi _{0.50}) _{1-x} In _x alloys; Atmosphere : Argon at pressure p = 0.1MPa, starting amount n _{Bi} = 0.001699 mol, n _{Sn} = 0.001699 mol, K = 0.00332 J μVs ⁻¹ , T _D = 298 K, T _M = 855 K, Δ _{mix} H _{Bi-Sn} = 127.43 J mol ⁻¹ , H _{ln} ^{T_D→T_M} = 19473.15 (J mol ⁻¹) [Kubaschewski and Alcock (1979)]							
0.000383	0.1013	0.0001	6.389	0.02	-1.069	-2791	-168.2
0.000476	0.2018	0.0001	8.16	0.02	-1.109	-2330	-409.9
0.000589	0.2988	0.0002	10.15	0.03	-1.319	-2239	-632.3
0.000847	0.4031	0.0002	14.59	0.04	-1.9	-2243	-871.9
0.001406	0.5213	0.0002	25.23	0.07	-2.145	-1526	-1001.4
0.001686	0.6132	0.0001	31.08	0.09	-1.755	-1041	-1009
0.005285	0.7585	0.0001	100.6	0.28	-2.332	-441.2	-795.7
0.005503	0.8264	0.0001	106.7	0.3	-0.473	-85.95	-596.2
0.005448	0.8642	0.0001	105.8	0.3	-0.34	-62.41	-480.0
0.00559	0.8890	0.0002	108.5	0.31	-0.303	-54.20	-402.2
0.005575	0.9061	0.0001	108.3	0.3	-0.229	-41.08	-346.6
Series 7: (Sn _{0.67} Bi _{0.33}) _{1-x} In _x alloys; Atmosphere : Argon at pressure p = 0.1MPa, starting amount n _{Bi} = 0.001238 mol, n _{Sn} = 0.002475 mol, K = 0.00370 J μVs ⁻¹ , T _D = 298 K, T _M = 767 K, Δ _{mix} H _{Bi-Sn} = 121.69 J mol ⁻¹ , H _{ln} ^{T_D→T_M} = 16906.14 (J.mol ⁻¹) [Kubaschewski and Alcock (1979)]							
0.000396	0.0964	0.0001	5.811	0.02	-0.884	-2232	-105.2
0.000568	0.2061	0.0001	8.656	0.03	-0.947	-1667	-294.9
0.000737	0.3142	0.0001	11.24	0.03	-1.219	-1654	-479.9
0.000807	0.4032	0.0001	12.31	0.04	-1.331	-1649	-631.6
0.001354	0.5098	0.0001	20.98	0.06	-1.911	-1411	-771.0
0.002033	0.6136	0.0001	32.84	0.09	-1.533	-754.1	-767.4
0.002845	0.7018	0.0002	46.83	0.14	-1.272	-447.1	-694.2

0.005496	0.7931	0.0002	91.77	0.28	-1.143	-208.0	-545.3
0.005466	0.8414	0.0002	91.65	0.27	-0.761	-139.2	-450.5
0.00562	0.8721	0.0001	94.42	0.29	-0.592	-105.3	-383.7
0.005414	0.8922	0.0001	91.01	0.27	-0.516	-95.31	-338.4
0.005612	0.9073	0.0001	94.9	0.28	0.024	4.277	-290.4
Series 8: (Sn _{0.67} Bi _{0.33}) _{1-x} In _x alloys; Atmosphere : Argon at pressure p = 0.1MPa, starting amount n _{Bi} = 0.001238 mol, n _{Sn} = 0.002475 mol, K = 0.00328 J μVs ⁻¹ , T _D = 298 K, T _M = 813K, Δ _{mix} H _{Bi-Sn} = 125.71 J mol ⁻¹ , H _{In} ^{T_D→T_M} = 18249.02 (J mol ⁻¹) [Kubaschewski and Alcock (1979)]							
0.000441	0.1062	0.0001	7.196	0.02	-0.852	-1932	-92.74
0.000584	0.2163	0.0001	9.7	0.03	-0.957	-1639	-283.3
0.000598	0.3042	0.0001	9.937	0.03	-0.976	-1632	-434.5
0.00096	0.4103	0.0002	15.96	0.05	-1.559	-1624	-615.8
0.001109	0.4986	0.0001	18.58	0.06	-1.66	-1497	-747.8
0.001907	0.6013	0.0002	33.37	0.11	-1.431	-750.4	-748.3
0.003238	0.7041	0.0002	57.66	0.20	-1.429	-441.3	-669.1
0.0051	0.7896	0.0002	92.27	0.30	-0.8	-156.9	-521.1
0.005161	0.8372	0.0001	93.5	0.31	-0.683	-132.3	-433.1
0.005559	0.8691	0.0001	101.1	0.33	-0.346	-62.24	-360.5
0.005452	0.8902	0.0001	99.27	0.33	-0.223	-40.90	-308.9
0.005393	0.9053	0.0001	98.54	0.32	0.123	22.81	-263.3
Series 9: (Sn _{0.67} Bi _{0.33}) _{1-x} In _x alloys; Atmosphere : Argon at pressure p = 0.1MPa, starting amount n _{Bi} = 0.001238 mol, n _{Sn} = 0.002475 mol, K = 0.00318 J μVs ⁻¹ , T _D = 298 K, T _M = 855 K, Δ _{mix} H _{Bi-Sn} = 128.00 J mol ⁻¹ , H _{In} ^{T_D→T_M} = 19473.15 (J mol ⁻¹) [Kubaschewski and Alcock (1979)]							
0.000434	0.1047	0.0001	7.709	0.02	-0.742	-1710	-64.32
0.000568	0.2125	0.0001	10.14	0.03	-0.919	-1618	-251.5
0.000592	0.3004	0.0001	10.54	0.03	-0.988	-1669	-409.6
0.000843	0.3963	0.0001	15.05	0.04	-1.363	-1617	-575.1
0.001434	0.5104	0.0001	25.9	0.07	-2.028	-1414	-733.7
0.001835	0.6058	0.0002	34.41	0.10	-1.327	-723.2	-731.7
0.003217	0.7062	0.0001	61.4	0.18	-1.248	-387.9	-644.2
0.005497	0.7952	0.0001	106.4	0.31	-0.661	-120.2	-485.3
0.005491	0.8428	0.0001	106.4	0.30	-0.541	-98.52	-395.4
0.005187	0.8711	0.0001	100.9	0.30	-0.124	-23.91	-328.5
0.005703	0.8924	0.0002	111.3	0.32	0.241	42.26	-267.3
0.005548	0.9073	0.0001	108.5	0.31	0.493	88.86	-218.0

^a Standard uncertainties u are: u(T_M) = 1 K, u(p) = 10 kPa, u(n_{Bi}) = 0.000001 mole, u(n_{Sn}) = 0.000001 mole, u(n_{In}) = 0.000002 mole, u(ΔH_{Reaction}) = 0.001 kJ; Series 1: u(K) = 0.00002 J μV s⁻¹, u(Δ_{mix}H) = 0.0233 kJ mol⁻¹; Series 2: u(K) = 0.00002 J μV s⁻¹, u(Δ_{mix}H) = 0.0197 kJmol⁻¹; Series 3: u(K) = 0.00002 J μVs⁻¹, u(Δ_{mix}H) = 0.01608 kJmol⁻¹; Series4: u(K) = 0.00001 J μVs⁻¹, u(Δ_{mix}H) = 0.01817 k J mol⁻¹; Series 5: u(K) = 0.00001 J μV s⁻¹, u(Δ_{mix}H) = 0.0144 kJ mol⁻¹; Series 6: u(K) = 0.00001 J μV s⁻¹, u(Δ_{mix}H) = 0.0127 kJ mol⁻¹; Series 7: u(K) = 0.00001 J μV s⁻¹, u(Δ_{mix}H) = 0.0132 kJ mol⁻¹; Series 8: u(K) = 0.00002 J μV s⁻¹, u(Δ_{mix}H) = 0.0105 kJ mol⁻¹; Series 9: u(K) = 0.00002 J μV s⁻¹, u(Δ_{mix}H) = 0.0079 kJ mol⁻¹.

^bT_D= Drop temperature in Kelvin, T_M= Bath temperature in Kelvin, n_{sn}= number of moles of Tin, n_{Bi}= number of moles of Bismuth, K= Calibration constant, Δ_{mix}H_{Bi-Sn}= Integral enthalpy of Binary Bi-Sn system, ΔH_{Signal} = It is the heat effect due to single drop of indium sample to the bath, Δ_{mix}H = it is the integral enthalpy of mixing of Bi-In-Sn system.

Generally, there are five sources of errors in the calorimetric data: i) construction of the calorimeter ii) calibration iii) integration of signal iv) incomplete dissolution v) presence of impurities. The overall experimental uncertainty of the calorimeter is 10-12 %. The error involved, in calibration of MHTC 96 line evo instrument (Setaram, France), by dropping NIST standard sapphire was estimated to be less than ± 1.5 %.

Enthalpies of mixing at 767, 813 and 855 K in the liquid In-Sn-Bi ternary system for three different cross sections are shown in Figures 2-4. It is observed that enthalpies of mixing in these three cross sections are exothermic in nature. These measured enthalpies show a systematic trend for all the compositions at different temperature. The segregation of atoms in this system is ruled out because there is no sudden increment or decrement of mixing enthalpies.

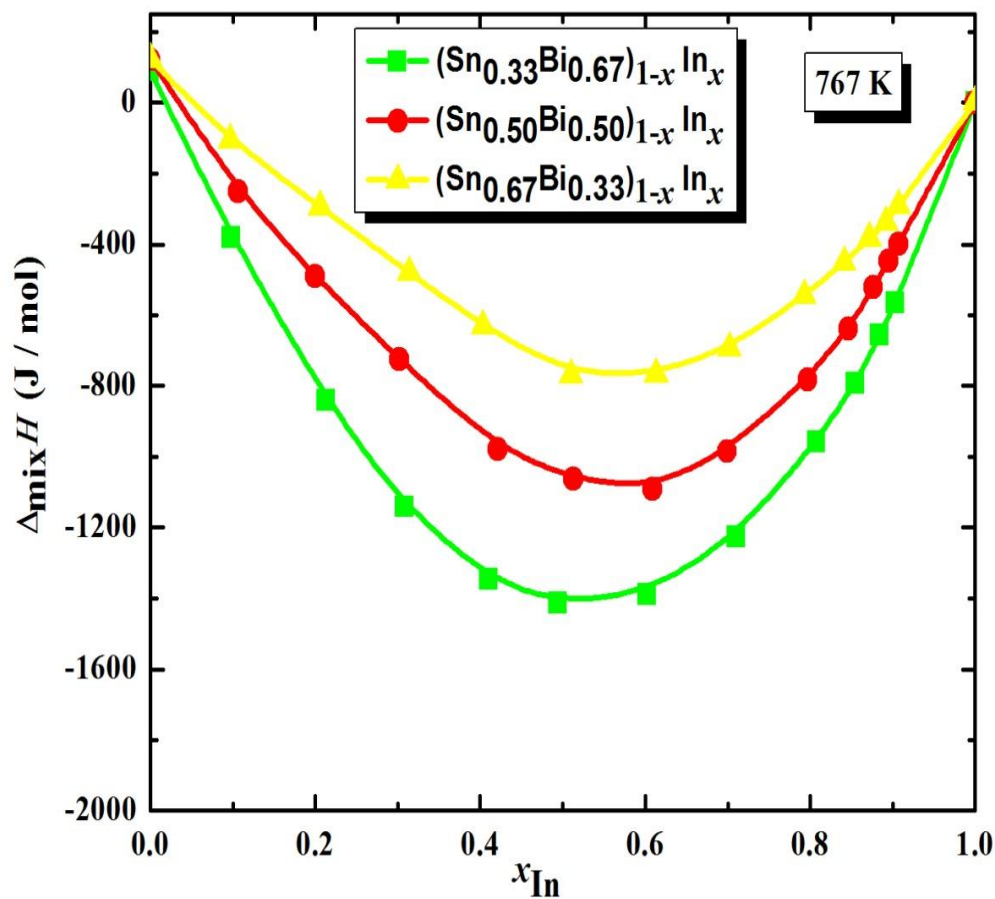


Figure 5.2 Integral molar mixing enthalpies of liquid Bi-In-Sn alloys along cross section of $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$; ■, $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x}\text{In}_x$; ● and $(\text{Sn}_{0.67}\text{Bi}_{0.33})_{1-x}\text{In}_x$; ▲ at 767 K.

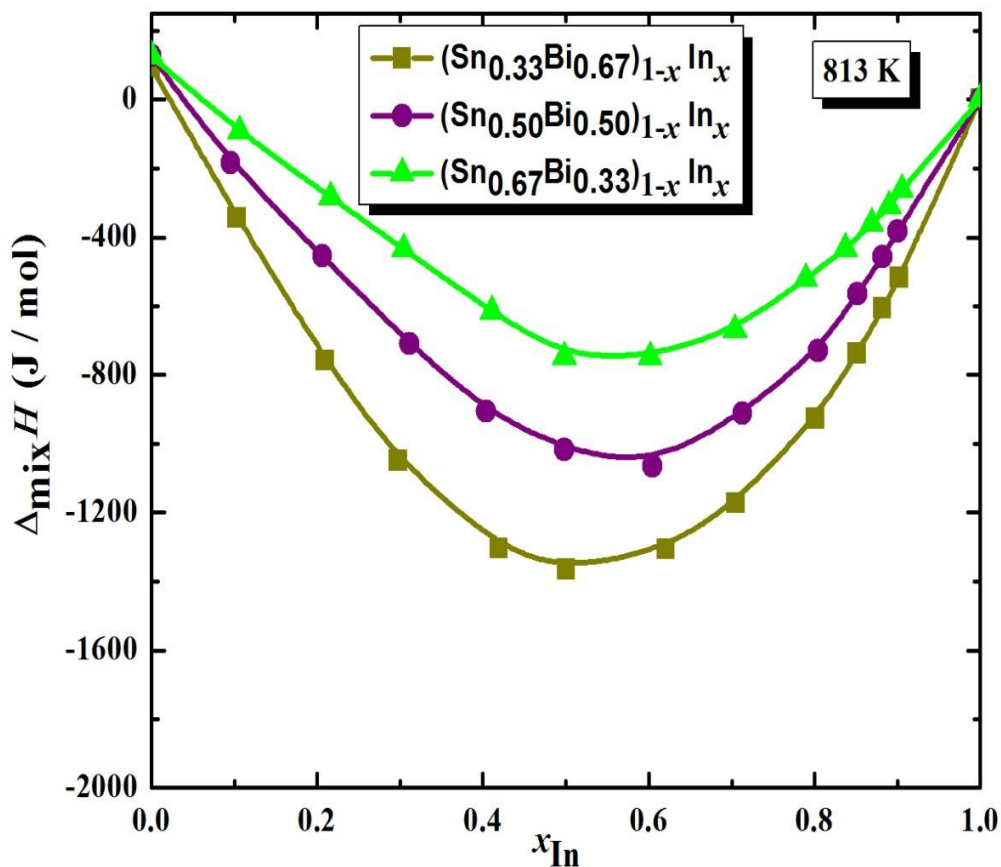


Figure 5.3 Integral molar mixing enthalpies of liquid Bi-In-Sn alloys along cross section of $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$; ■, $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x}\text{In}_x$; ● and $(\text{Sn}_{0.67}\text{Bi}_{0.33})_{1-x}\text{In}_x$; ▲ at 813 K.

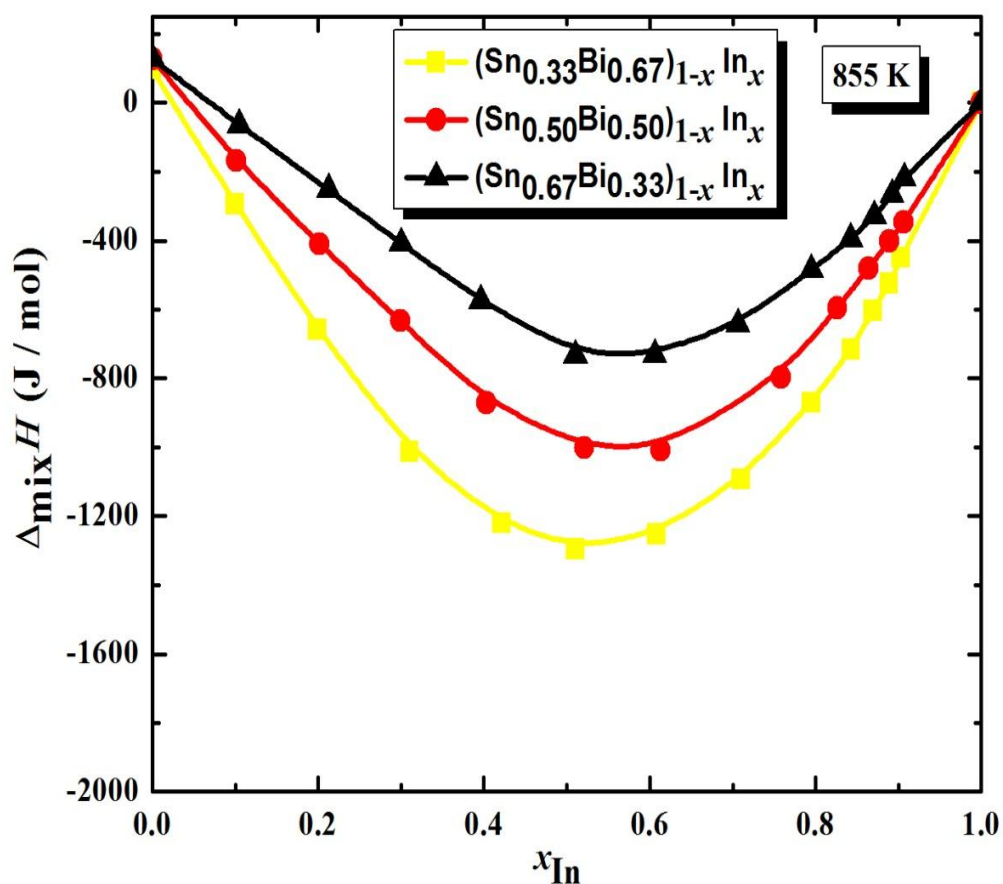


Figure 5.4 Integral molar mixing enthalpies of liquid Bi-In-Sn alloys along cross section of (Sn_{0.33}Bi_{0.67})_{1-x}In_x; ■, (Sn_{0.50}Bi_{0.50})_{1-x}In_x; ● and (Sn_{0.67}Bi_{0.33})_{1-x}In_x; ▲ at 855K.

It is observed that the nature of variation of enthalpies of mixing with indium composition is similar in Fig. 5.2-5.4. The minima for the enthalpy of mixing for the cross sections $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x}\text{In}_x$ and $(\text{Sn}_{0.67}\text{Bi}_{0.33})_{1-x}\text{In}_x$ are close to $x_{\text{In}} = 0.6$ and whereas for the cross section $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$, it is almost symmetric. As indium content increases enthalpies of mixing decreases and it approaches to a minimum at $x_{\text{In}} = 0.55$ and again increases towards zero. It could also be inferred that there is no chance of compound formation in this system due to absence of strong interaction amongst the atoms in this ternary system. It has also been observed that the minima in enthalpy of mixing curve become less exothermic as $x_{\text{Sn}}/x_{\text{Bi}}$ ratio increases. It is maximum at equiatomic percent and diminishes at terminal ends. It could be due to change of entropy of mixing by the change of temperature. Enthalpy of mixing contributes negatively to the Gibbs energy irrespective of the sign of the entropy of mixing. The observed negative enthalpy of mixing inferred that finite interatomic interaction energy is present amongst atoms in this system. This energy is being released in the process of mixing confirmed by the exothermic nature of the heat of mixing. From Figures 5.5-5.7, it could also be observed that the plots are very close to each other at 767, 813 and 855 K. It may be interpreted that the enthalpy of mixing in Bi-In-Sn system is almost independent of temperature.

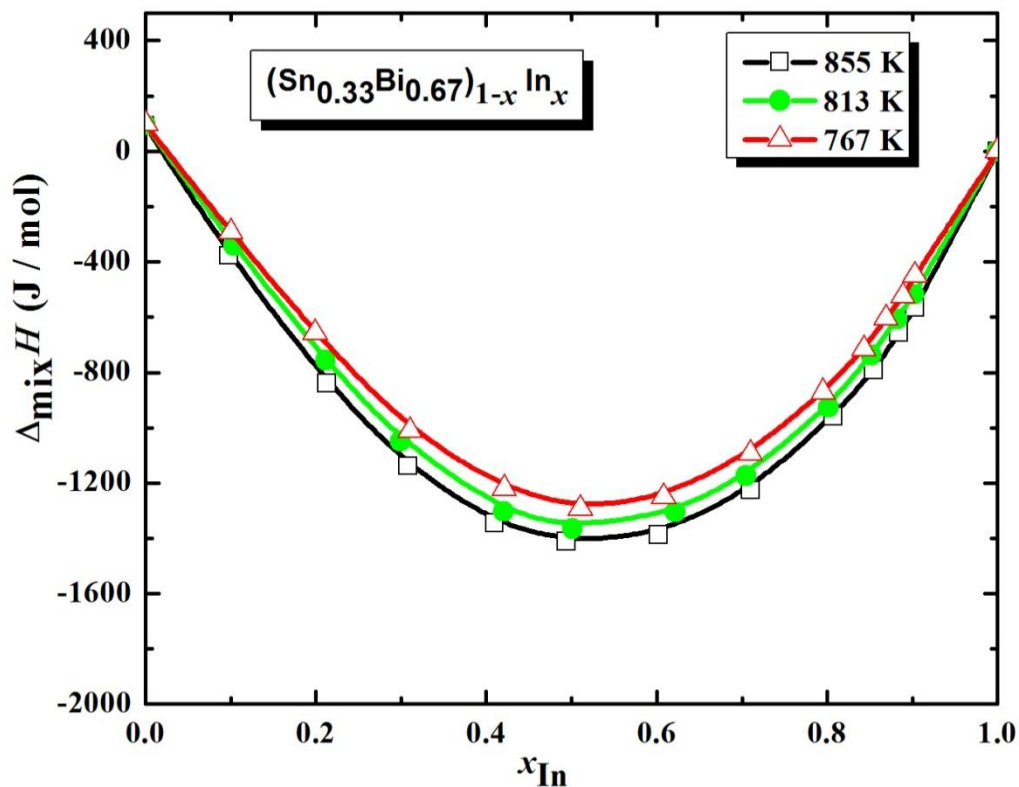


Figure 5.5 Integral molar mixing enthalpies of liquid Bi-In-Sn alloys along cross section of $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$ at 767 K; \square , 813 K; \bullet and 855 K; \triangle , — trend line, standard states: pure liquid metals.

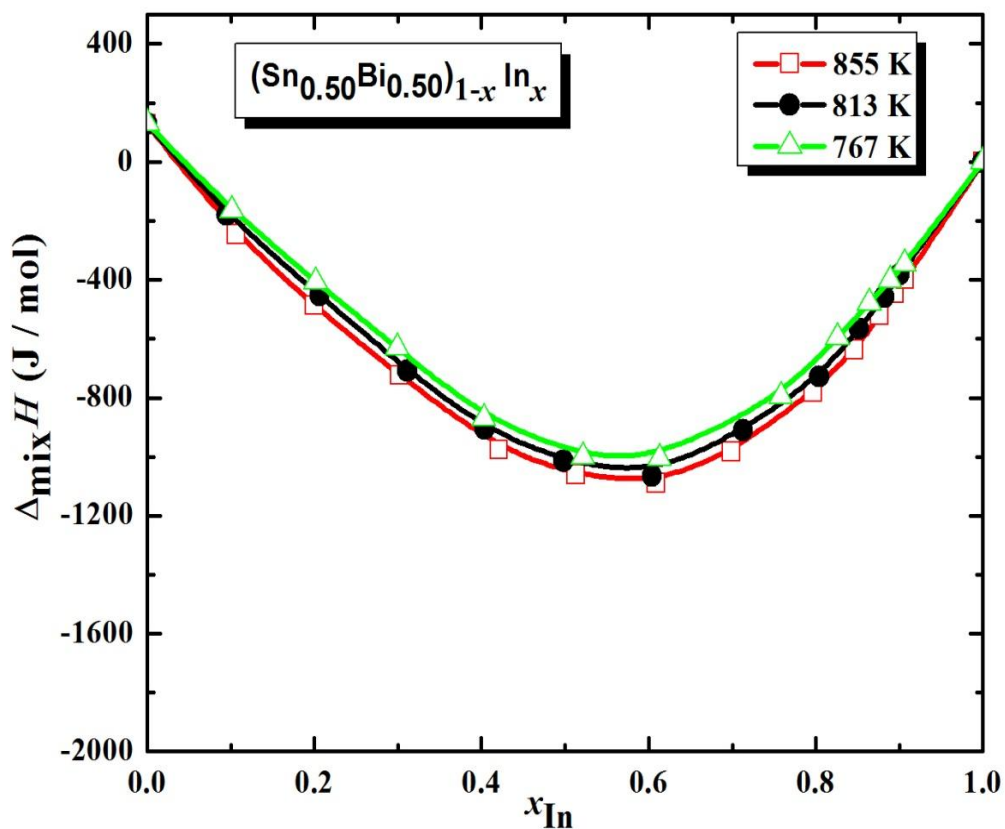


Figure 5.6 Integral molar mixing enthalpies of liquid Bi-In-Sn alloys along cross section of $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x}\text{In}_x$ at 767 K; \square , 813 K; \bullet and 855 K; \triangle , — trend line.

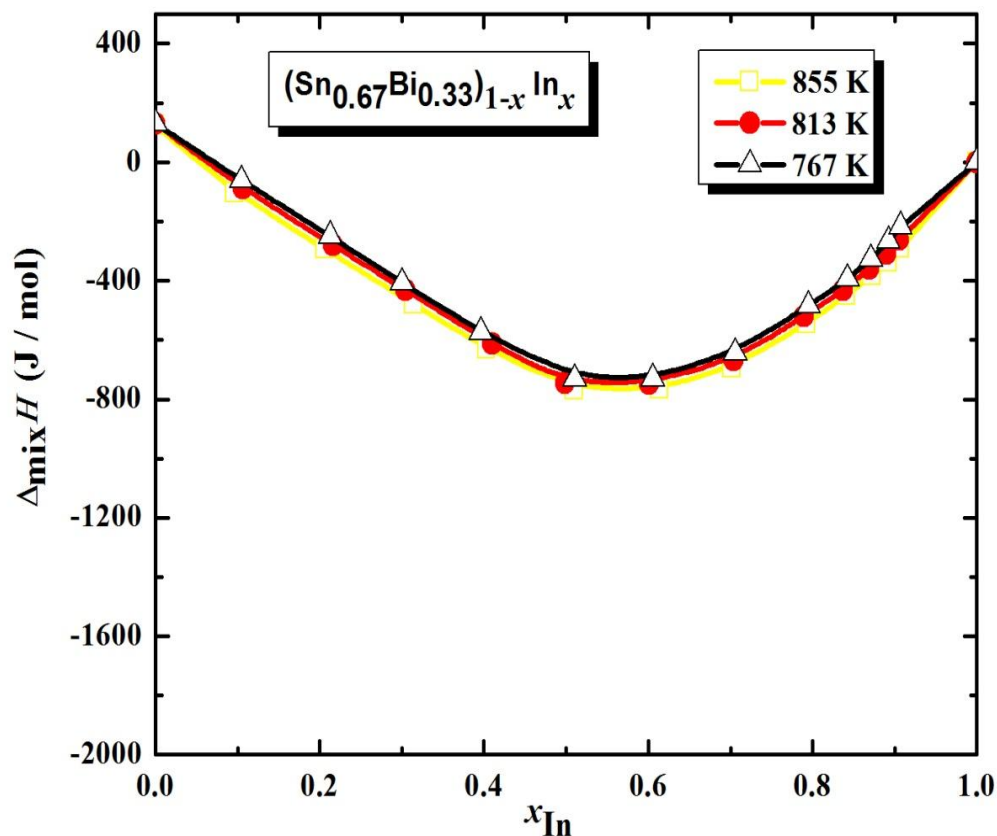


Figure 5.7 Integral molar mixing enthalpies of liquid Bi-In-Sn alloys along cross section of $(\text{Sn}_{0.67}\text{Bi}_{0.33})_{1-x}\text{In}_x$ at 767 K; \square , 813 K; \bullet and 855 K; Δ , — trend line.

The comparison of mixing enthalpy value of Brunetti et al. [Brunetti et al. (2006)] with our experimental data is presented in the Figure 5.8. Only one of the mixing enthalpy values is compared with the data from this study. It was observed that the mixing enthalpy of Brunetti et al. is slightly more negative as compared to our data. It may be due to different in the temperature of measurement and composition of the alloy does not match exactly with our compositions.

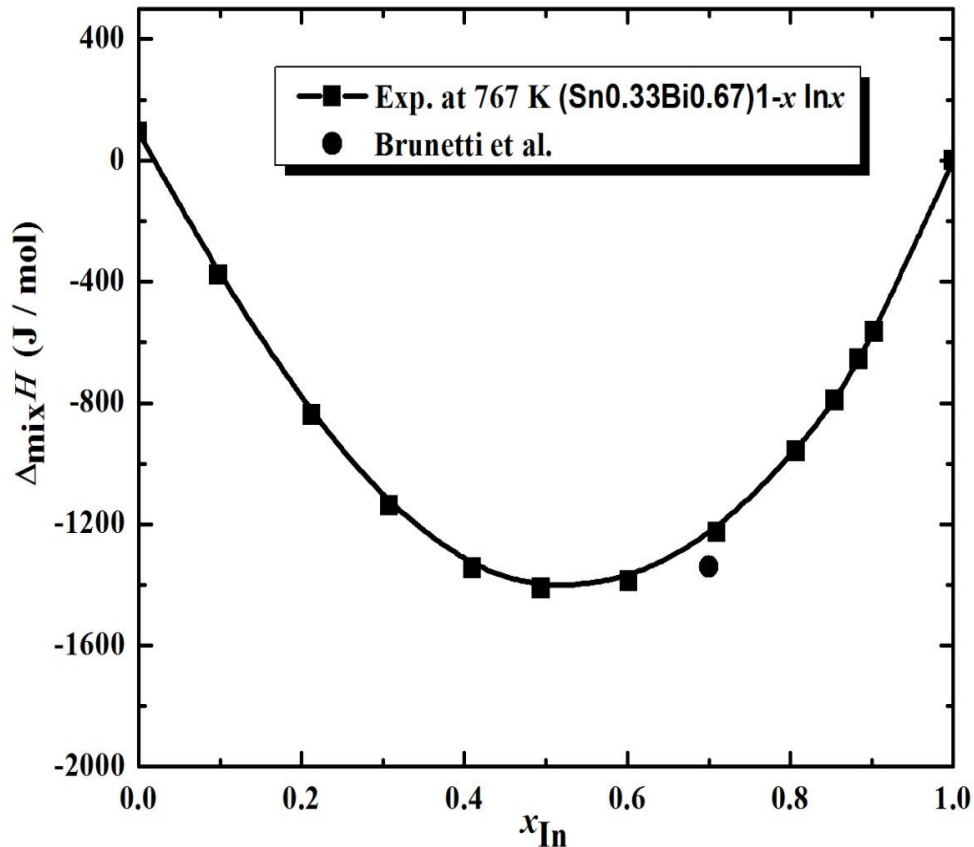


Figure 5.8 Comparison of integral molar mixing enthalpies of liquid Bi-In-Sn alloys along cross section: $(\text{Sn}_{0.33}\text{Bi}_{0.67})_{1-x}\text{In}_x$; ■, at 767 K (this study) and Brunetti et al.(2006) ; ▲.

5.5 Iso-enthalpy curves for the integral enthalpy of mixing

The compositions of In, Bi and Sn along different cross sections were determined by plotting graph at 813 K with Bi-In and In-Sn and selecting the intersection points of horizontal enthalpy lines and integral mixing enthalpy curves. The compositions values with respect to these intersection points are given in Table 5.3. By using the data points of Table 5.3 iso-enthalpy curves for integral enthalpy of mixing are drawn on ternary

(Bi-In-Sn) compositional diagram. The iso enthalpy curves along integral mixing enthalpy values of -200, -600, -1000 and -1400 J/mole at 813 K are shown in Figure.

4.9.

Table 5.3 Compositions of In, Bi and Sn against different integral enthalpy values

$\Delta_{mix}H$ (J/mole)	X_{Sn}	X_{In}	X_{Bi}
-200	0	0.0413	0.9587
	0.3144	0.0568	0.6288
	0.46115	0.0777	0.46115
	0.59153	0.1127	0.29577
	0.7299	0.2701	0
	0.1218	0.8782	0
	0.04533	0.932	0.02267
	0.024	0.952	0.024
	0.01333	0.96	0.02667
	0	0.969	0.031
-600	0	0.1243	0.8757
	0.28332	0.1501	0.56658
	0.38765	0.2247	0.38765
	0.43706	0.34423	0.21871
	0.1588	0.7618	0.0794
	0.0773	0.8454	0.0773
	0.04117	0.87649	0.08234
	0	0.8867	0.1133
-1000	0	0.2145	0.7855
	0.2445	0.2665	0.489
	0.28635	0.4273	0.28635
	0.1624	0.6752	0.1624
	0.07643	0.7707	0.15287
	0	0.7814	0.2186
	0	0.7814	0.2186
-1400	0	0.32119	0.67881
	0.16667	0.5	0.33333
	0	0.644	0.356

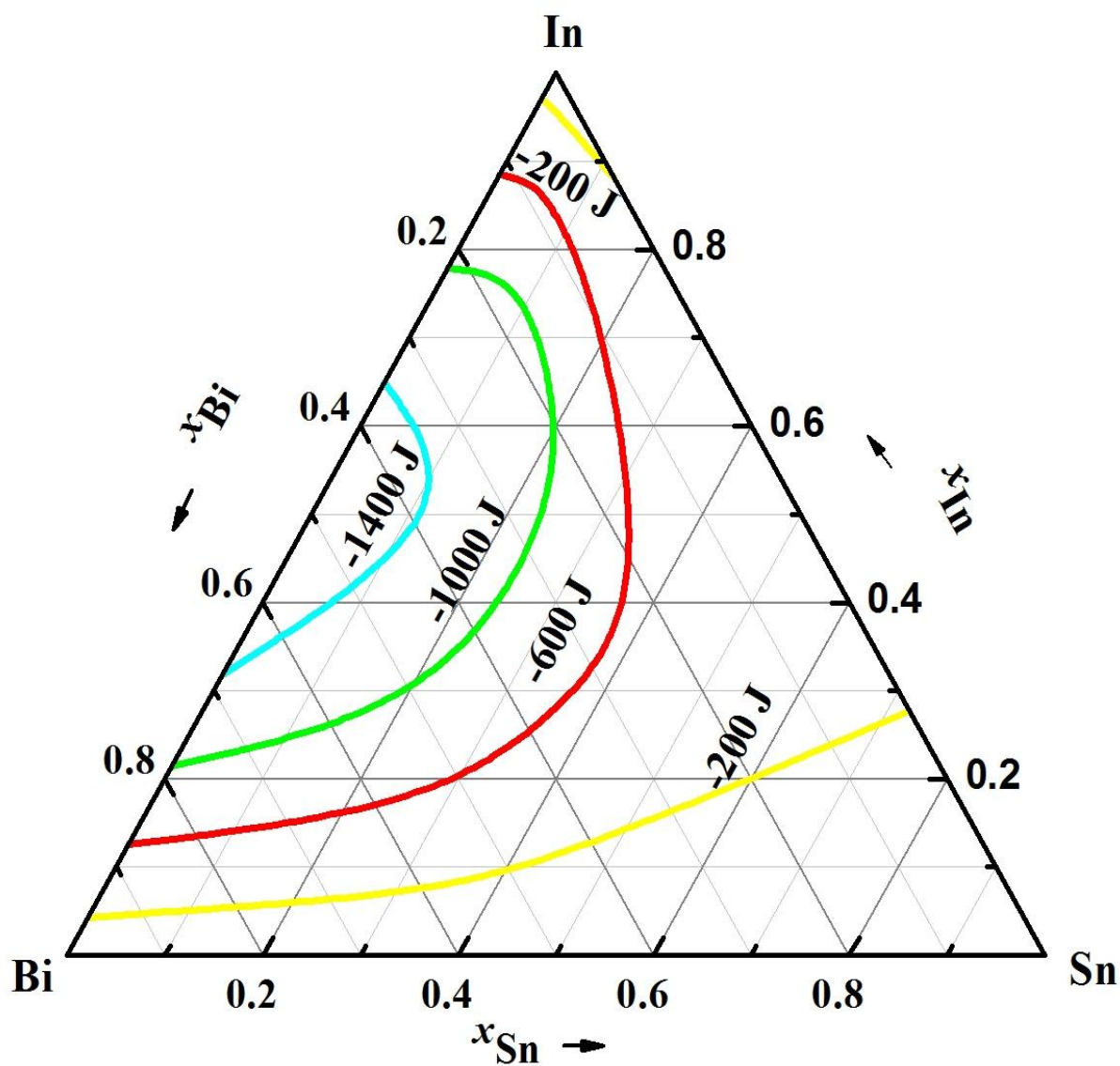


Figure 5.9 Iso-enthalpy curves of liquid Bi-In-Sn alloys at 813 K; reference states: pure liquid metals, values are in J/mol

From the Figure 5.9, it is observed that the negative values of integral mixing enthalpy are predominant inside the ternary triangle. It could be inferred that there is not a strong interactions among the indium, tin and bismuth atoms in the solutions because the integral enthalpy values are not so highly negative. The maximum negative value of integral mixing enthalpy is -1.4 KJ/mole. It is clear from the Figure 5.9 that integral enthalpy of mixing decreases as the curves shift towards In-Bi binary system. All the curves start from In-Bi line, moves towards In-Sn line and come back to the In-Bi line. It implies that the In-Bi binary system has more influence on ternary system as compared to In-Sn and Bi-Sn. From the Figure 5.9, we can also say that Sn has the less influence on Bi-In-Sn ternary system as compared to In and Bi.

5.6 Theoretical Modeling

There are various theoretical models available to predict the thermodynamic properties of the ternary and higher order systems from the boundary binary data. One of the important theoretical models has been proposed by Ansara and Dupin [Ansara and Dupin (1998)]. It has also been used by Luef et al [Luef et al. (2005)] using Redlich - Kister - Muggianu polynomial for substitutional solutions. The experimental data were treated with the least square fit as per the equation. (4.1).

$$\Delta_{mix}H = \sum_i \sum_{j>i} \left[x_i x_j \sum_v L_{i:j}^{(v)} (x_i - x_j)^v \right] + x_i x_j x_k \left(L_{i:j:k}^0 x_i + L_{i:j:k}^1 x_j + L_{i:j:k}^2 x_k \right) \dots \dots \dots (5.1)$$

Where $L_{i:j}^{(v)}$ ($v = 0, 1, 2,$) are the binary interaction parameters of the boundary binary systems and $L_{i:j:k}^{(v)}$ ($v = 0, 1, 2$) are the ternary interaction parameters. The additional enthalpy mixing is resulting from the ternary interactions in this system. Ternary enthalpy of mixing for Bi - In-Sn systems for the section $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x} \text{In}_x$ is

represented in Fig. 5.10 along with least square fit curve at 813 K as per the equation. (5.1).

The ternary interaction parameters are obtained from the experimental results. The binary interaction parameters were taken from Chapter 4. The binary and ternary interaction parameters are listed in the Table 5.4. It has been observed that the calculated curve obtained from the binary and ternary interaction parameters is very close to the experimental results except some of the values of enthalpy of mixing for indium rich compositions. The deviations are within the error limit of the experimental results.

Table 5.4 Binary and ternary interaction parameters

Interaction parameter	ν	(J/mol)
$L_{\text{Bi-In}}(\nu)$	0	-6617
	1	133
	2	2066
$L_{\text{Bi-Sn}}(\nu)$	0	520
	1	235
	2	-157
	3	-119
$L_{\text{In-Sn}}(\nu)$	0	-1980
	1	-893
$L_{\text{Bi-Sn-In}}(\nu)$	0	-3874
	1	-12777
	2	24187

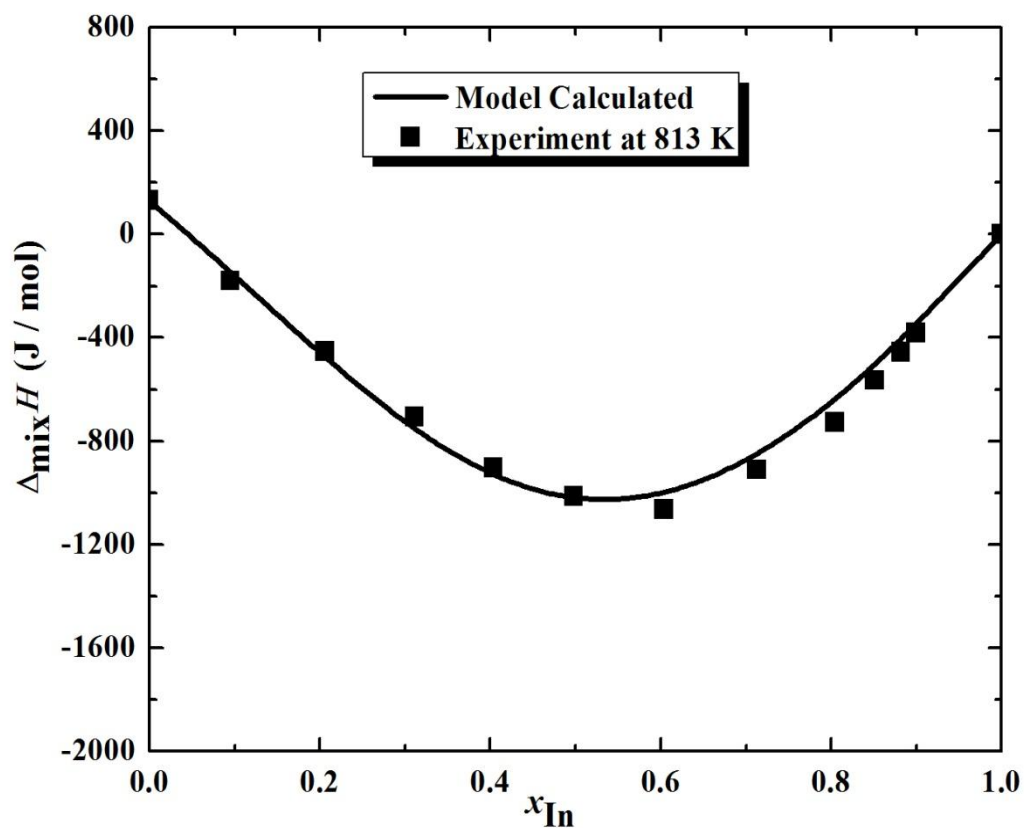


Figure.5.10 Comparison of integral molar mixing enthalpies between theoretical model; — and this study at 813 K for $(\text{Sn}_{0.50}\text{Bi}_{0.50})_{1-x}\text{In}_x$ alloys; ■